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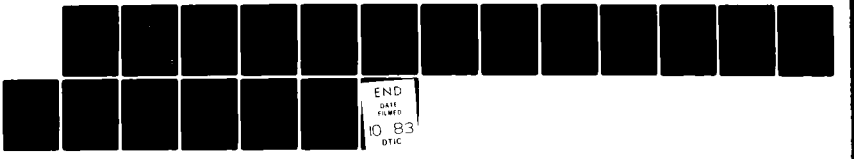

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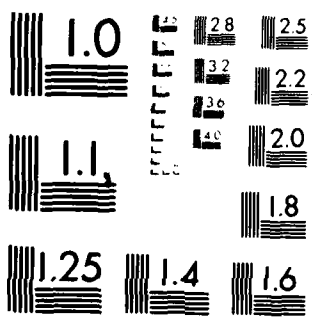

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BASIC VISION EVENTS

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1 AUGUST 1982

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This investigation studied basic visual events in three particular areas. First, additional physical explanations for visual sensitivity at 589 nm have been obtained which suggests that there may be other monochromatic wavelengths with high visual sensitivity. Second, new femtosecond lasers have been applied to elucidate new, unresolved primary processes in visual transduction. Third, fundamental mechanisms in a unique, rapidly adjustable light filter based on molecules used in visual systems have been studied.

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PROGRESS REPORT

During the past year considerable progress has been made in three areas which cover a variety of subjects of potential interest to the Naval Air Systems Command. First, we have obtained an additional physical explanation for visual sensitivity at 589 nanometers (nm) which suggests that there may be other monochromatic wavelengths with high visual sensitivity. Second, we have applied new femtosecond lasers to elucidate new unresolved primary processes in visual transduction. Third, we have been studying fundamental mechanisms in a unique radidly adjustable light filter based on molecules used in visual systems.

FUNDAMENTAL STUDIES OF VISUAL SENSITIVITY AT 589 nm

Over the last year as a result of research under our contract with the Naval Air System Command, we have been able to determine the vibrational modes stimulated in the visual chromophore by monochromatic emissions of interest to the United States Navy. Such studies are particularly important in developing an understanding of visual sensitivity control at these wavelengths. Our data has helped us arrive at an additional physical explanation for sensitivity at 589 nm. First, the data will be reviewed and then the conclusions will be summarized.

In Table I a list of the vibrational modes observed for the different double bond isomeric forms of the visual chromophore are reproduced for monochromatic yellow light at 589 nm. The descriptions of these modes were gleaned from a variety of chemically modified retinals. Principally, several major groups of bands are observed beginning with the C-H bending vibration of chain vinyl hydrogens around ~960 cm^{-1} (Δ cm^{-1} from laser). This is followed by $C=Ch_3$ stretching modes at ~1010 cm^{-1} arising from the C_9 and C_{13} positions and the region between ~ 1100 – ~1200 cm^{-1} known as the fingerprint region. The fingerprint region is composed of C-C/C=C stretching modes which are very sensitive to the configuration of the isoprenoid chain both in terms of the relative intensity and frequency of the vibrational modes. In Schiff bases (i.e., X=N) there is an additional mode between ~1220 – ~1250 cm^{-1} which is dependent on the state of protonation of the nitrogen and exhibits frequency alteration in concert with the C=N vibrational frequency. The next higher frequency mode occurs at ~1272 cm^{-1}. This mode occurs with varying intensity in most retinal type molecules. It appears, however, that this mode exhibits its largest intensity when the chromophore is in an 11-cis configuration. Between ~1300 and 1475 cm^{-1} there are a whole series of weak bands. Our data show that the band in 11-cis retinal at 1345 cm^{-1} is altered by temperature and chemical modification in a way that indicates it is sensitive to the presence of 12-s-cis and 12-s-trans conformers that this isomer is capable of attaining. The most prominent band in the spectrum follows this group of weak vibrational structure. Our data clearly indicate that this mode is due to the C=C stretching vibration. In a number of cases the mode is split into several components. In addition to the above, the C=C stretching frequency generally seems to follow the absorption maximum of the chromophore and thus protonated membrane bound components have frequencies ranging ~1525 to ~1545 cm^{-1}, protonated isolated (unbound) chromophores ~1555 cm^{-1}, unprotonated bound chromophores from possibly as low as ~1550 to 1570 cm^{-1} and free retinals and unbound unprotonated chromophores between ~15700 and 1580 cm^{-1}. Finally, one observes one of the weakest vibrational modes in the spectrum. This mode, which has provided a wealth of information, occurs between ~1620 and 1655 cm^{-1} and corresponds to the -C=X stretching mode where X is 0 or N, a protonated or unprotonated Schiff base. For these species the vibrational frequencies are, respectively, ~1656 cm^{-1}, 1642-1655 cm^{-1} and ~1620 cm^{-1}.

Table 1. Suggested Vibrational Assignments Frequencies (cm^{-1})

Description of the Vibration*	Trans			13 - cis			11 - cis			9 - cis		
	C=X:	C=O	C=N	C=N (H)	C=O	C=N	C=N (H)	C=O	C=N	C=N (H)	C=O	C=N	-C=N- (H)
C=X stretch		1656	1622	1655	1659	1622	1654	1658	1618	1655	1656	1623	1658
C=C stretch		1577	1582	1555	1584	1585	1565	1576	1579	1557	1586	1588	1606
		1568			1573								1567
													1557
C_9 & C_{13} assymetric methyl deformation		1448[CCl_4]	[1]	[3]	1448[CCl_4]	[3]	[3]	1448[CCl_4]	[1]	1438	1446[CCl_4]	[1]	[3]
C_9 symmetric methyl deformation		1388[CCl_4]	[1]		1399[CCl_4]	1314		1387[CCl_4]	[1]		1402[CCl_4]	[1]	
											1374[CCl_4]	[1]	[3]
C_1 gem-dimethyl		1387[IR]	[2]	[2]	1380[IR]	[2]	[2]	1375[IR]	[2]	[2]	1379[IR]	[2]	[2]
		1362[IR]	[2]	[2]	1362[IR]	[2]	[2]	1358[IR]	[2]	[2]	1360[IR]	[2]	[2]
C_{13} symmetric methyl deformation		1337	1327		1352	1331	1323	1345	[3]	[3]	1337	1327	1327
					1316	1309					1329		
C-C-N bend + C=C stretch		1282	1284	1282	1282	[3]	1274	1271	1272	1272	1295	[3]	1294
or C-C stretch		1272	1272	1272	1274						1200		1273
C-C stretch, CH_3 rock			1222	1237	1222	1226	1238	1219	1220	1234	1216	1224	1238
		1198	1198	1193	1193	1198	1220	1206	1210	1212	1201	1203	1206
							1203			1200	1187		
			1178							1190			1191
C-C (C_9 to C_{13}) stretch		1163	1170	1159	1163	1163	1168				1147		
			1155					1143				1140	1140
C_{14} - C_{15}					1118			1128			1117	1125	
C_9 - CH_3 stretch		1009	1011	1007	1012	1012	1011	1017	1020	1012	1009	1007	1008
C_{13} - CH_3 stretch								997	1010	998			
C-C-N bend, out-of-plane		970	[3]	965	969	[3]	972	970	968	965	963	[3]	965

In summary an overview of these results provides a striking view of possible additional reasons for the sensitivity of the eye to 589 nm light. The data at this wavelength indicate a pattern of vibrational modes which is characteristic for rapid vibrational deactivation. Based on the data in Table I and our analysis we feel we have a unique explanation for 589 nm sensitivity. Thus we should now be able to survey and fingerprint various other monochromatic sources. Our data indicate that there should be other emissions that would give similar sensitivity.

UNRESOLVED PRIMARY PROCESS IN VISUAL TRANSDUCTION

The most probable description of the primary events in visual transduction is that light not only alters the retinal conformation but also causes excited and ground state protein conformational changes. A pictorial description of the suggested sequence of events for rhodopsin is reproduced from a paper by this author (1) and is seen in Figure 1. In this figure the states R, R*, P_x and Batho represent, respectively, rhodopsin, vertically excited rhodopsin, excited rhodopsin in the excited state minimum and the primary photochemical product bathorhodopsin which stores 12 Kcal of the light energy in an altered and separated R-R' salt linkage. Thus, electron motion in the isoprenoid molecular wire is coupled to proton movement in the protein. Retinal structural alteration keeps R and R' separated and a definite retinal structural alternation is suggested with double bond twists around the 9-10 and 11-12 double bonds. Nearly universal agreement has been achieved on ground state protein structural alteration and excited state retinal structural alteration. Arguments for excited and ground state retinal structural alteration (1) seen in Figure 1 can readily be made on the basis of photoreversibility and by experiments showing that the L thermal intermediate will directly and thermally revert to rhodopsin at appropriate temperature. Arguments for ground state protein structural alteration can be made based on D_2O psec experiments (1). However, arguments for excited state protein motion have only recently been demonstrated as part of the research done under this contract during the past year.

In order to demonstrate such excited state protein motion, we have used a ring dye laser system of the design recently reported by Shank et al (2). This system produces 100×10^{-15} sec (100 fsec) pulses at a wavelength of 619 nm. The pulses emanate from a mode-locked colliding ring dye amplifier pumped by a frequency doubled Nd:YAG laser. The pump probe technique was used where the pulse train is split into two beams (see Figure 2) with the pump pulse going through a chopper and the probe pulse being delayed relative to the pump by a variable delay stepping motor. The data obtained is seen in Figure 3. The dashed curve is the autocorrelation of the pulse showing its 100 fsec character. The solid curve is rhodopsin in H_2O which shows a time delay of 1.5 psec for the onset of the primary photochemical species after light strikes the sample. The dotted curve is rhodopsin in D_2O. This yields the fascinating result that in D_2O a more rapid rise time is obtained. This is clearly a most significant result that reaches to the very heart of the primary photochemical act in vision. It is also a most surprising result, which at present cannot be understood but will be probed in detail during the coming contract year.

FUNDAMENTAL MECHANISMS OF A RAPIDLY ADJUSTABLE MOLECULAR LIGHT FILTER

In several color vision systems natural filters in the form of oil droplets cover the photoreceptor cells. These natural filters are formed of carotenoids and have severely altered absorption properties (3). These observations and additional work done in our laboratory suggested to us that the fundamental properties of carotenoid suspensions may provide important clues as to how we might develop a molecular light filter with the ability to rapidly alter its absorption properties.

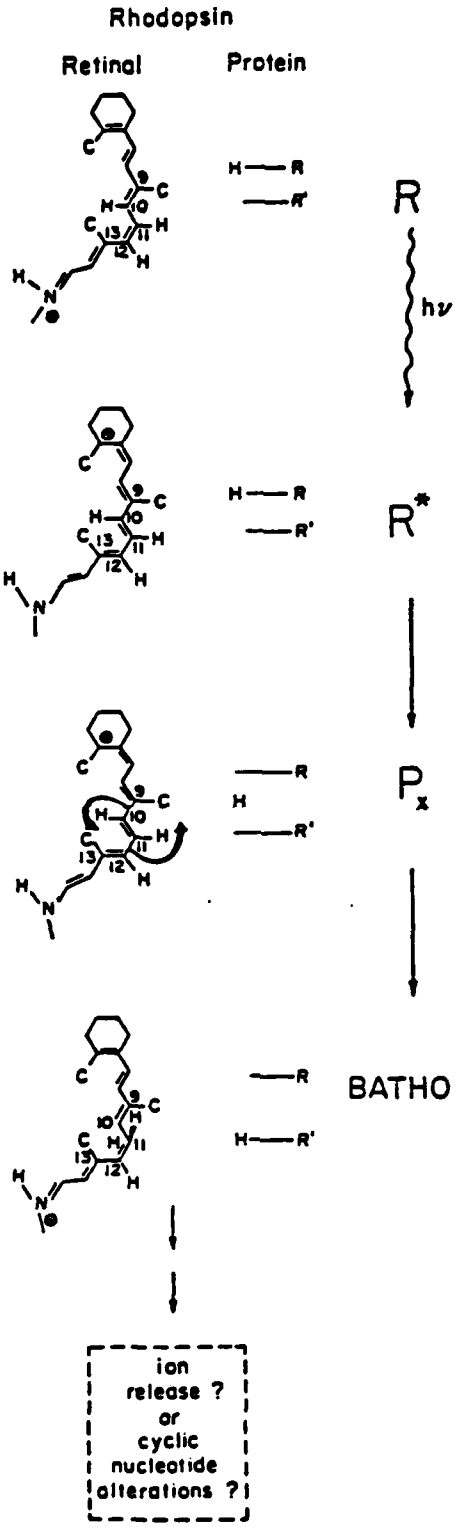

Figure 1. Sequence of Events for Rhodopsin

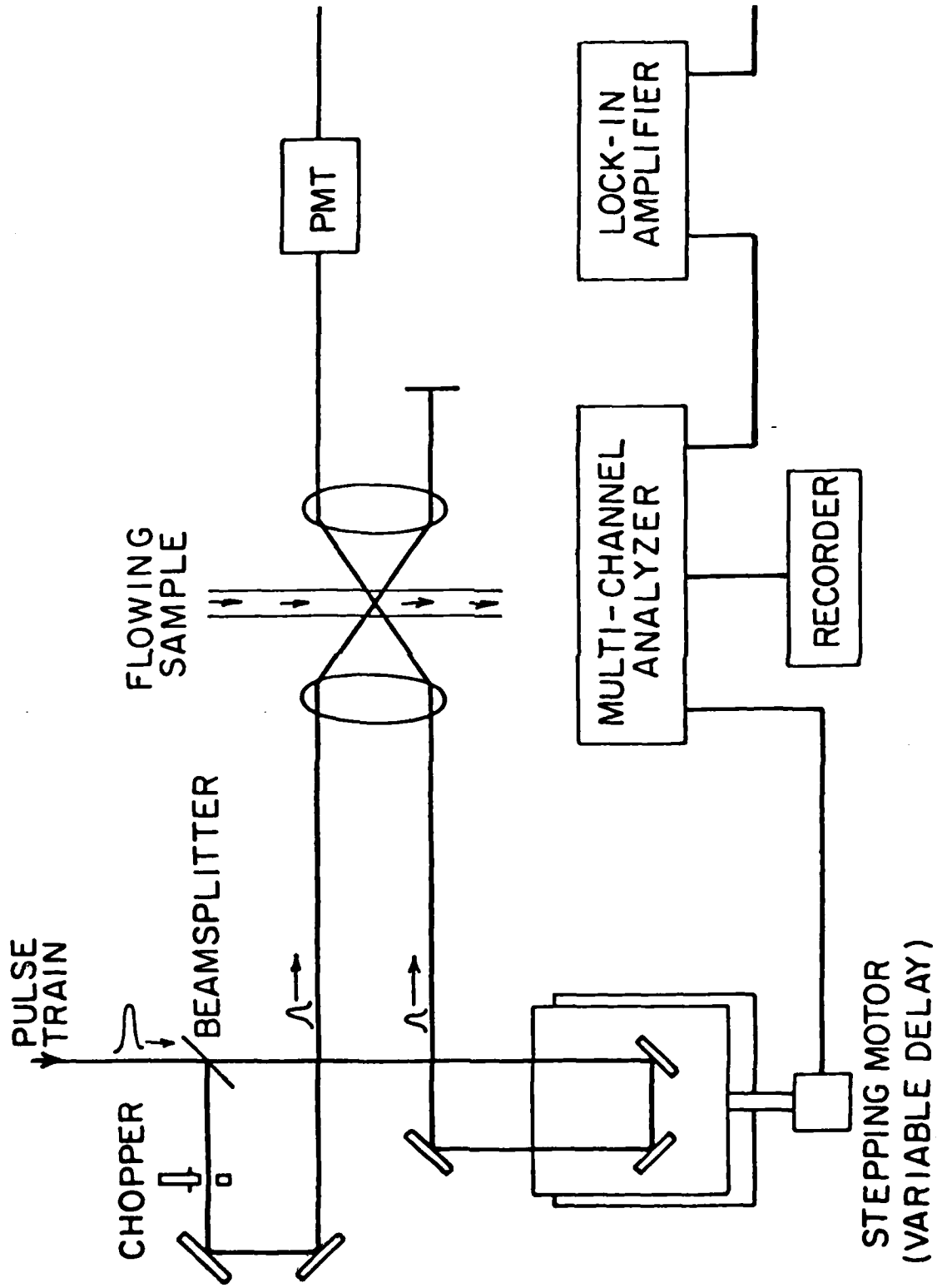

Figure 2. Ring Dye Laser System

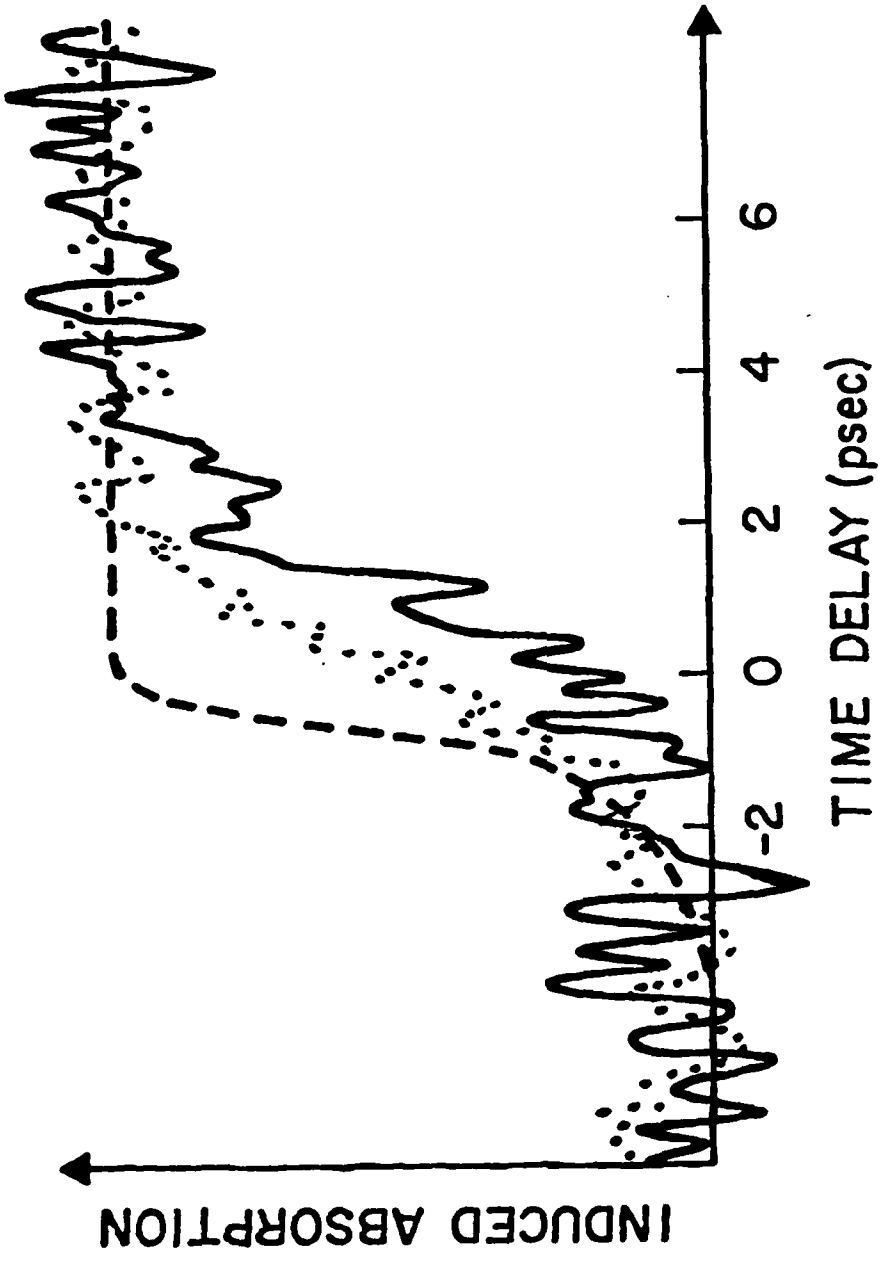

Figure 3. Ring Dye Laser System Data

Initial results in our laboratory showed that carotenoid suspensions decreased their light transmission over a broad range when illuminated with picosecond (psec) pulses at a variety of wavelengths. The molecular origin of these rapid light induced alternations in carotenoid absorption are being clarified as a result of our resonance Raman measurements of such systems over the past year.

These measurements on the carotenoid, astaxanthin, showed an alteration in the C=C stretching vibration from 1517 cm^{-1}, under the action of a 1.06μ, 30 mJ, 150 psec pulse, to 1524 cm^{-1} without psec excitation. In order to appreciate the molecular origin of these alterations in the resonance Raman spectrum of astaxanthin, consider the spectrum seen in Figure 4 which is of a $CC1_4$ solution of astaxanthin under the action of a 30 mJ, 150 psec pulse at 1.06μ. All observed bands are typical of carotenoids (2) and the strong vibrational mode at 1517 cm^{-1} is the C=C stretching vibration. This vibrational mode and those observed at 1007 cm^{-1}, 1158 cm^{-1}, 1186 cm^{-1} and 1214 cm^{-1} are common to most carotenoids. The scattering at 1272 cm^{-1} is typical to astaxanthin.

Figure 5 is the excitation profile of the most prominent Raman line of the same solution discussed above under the action of the psec pulse. There is no maximum, but an increase in intensity towards lower wavelengths. It has been shown (4) that the 0-0 transition makes the major contribution to the intensity enhancement of the Raman fundamentals, while the absorption maximum has additional contributions from 0-1, 0-2, 0-3 transitions, so that the maximum of the excitation profile occurs about 1600 cm^{-1} to the long wavelength side of the absorbance peak. The presence of excited state interactions which appear upon aggregation of the molecules, modifies the vibronic structure of the absorption band so that is consists of only the 0-0 transition. The absence of a maximum in Figure 5 at about 5200 Å indicates the presence of aggregates. Without the simultaneous illumination of the sample with the psec pulse a normal maximum is seen at 5200 Å. Thus, the above data strongly suggests that the molecular origin of the psec induced absorption changes is excited state interactions in molecular aggregates.

Table II lists the position of the C=C stretching mode $V_{C=C}$ for various excitation wavelengths with simultaneous illumination of the sample with a 1.06μ psec pulse. For carotenoids the vibrational frequency should be 1523 cm^{-1} for astaxanthin (4). It has been observed that these vibrational frequencies shift down by 5-6 cm^{-1} upon aggregation. For a mixture of monomers and different size aggregates, $V_{C=C}$ is given by:

$$V_{C=C}(\lambda) = \sum_{n=1}^{N} V_{C=C,n} * I_R(n,\lambda)$$

where $V_{C=C,n}$ is $V_{C=C}$ for an aggregate of n molecules, $I_R(n,\lambda)$ is the Raman intensity for an aggregate of n molecules at excitation wavelength λ, and the summation is over all possible sizes. Thus, it appears that the solution under the action of a psec pulse shows evidence for a large ratio of aggregates. Without the action of the psec pulse the C=C stretch exhibits no change as a function of the laser frequency that excites the Raman spectrum.

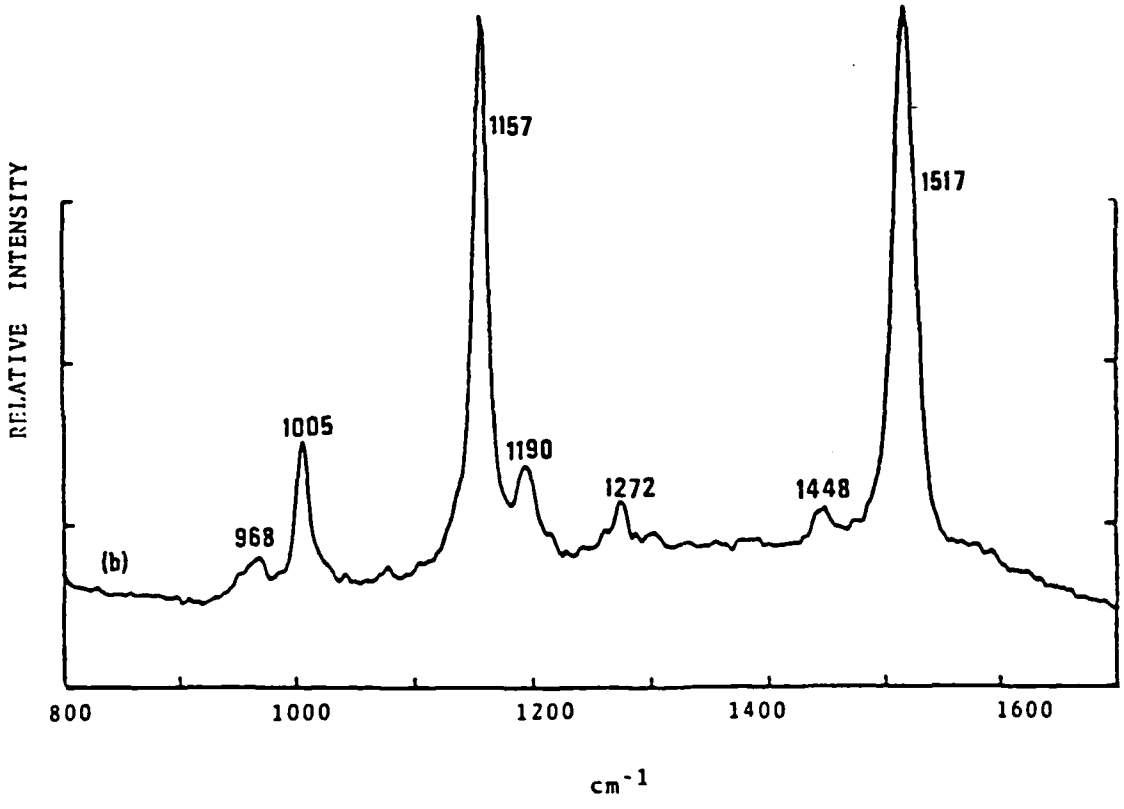

Figure 4. Resonance Raman Spectrum of Astaxanthin

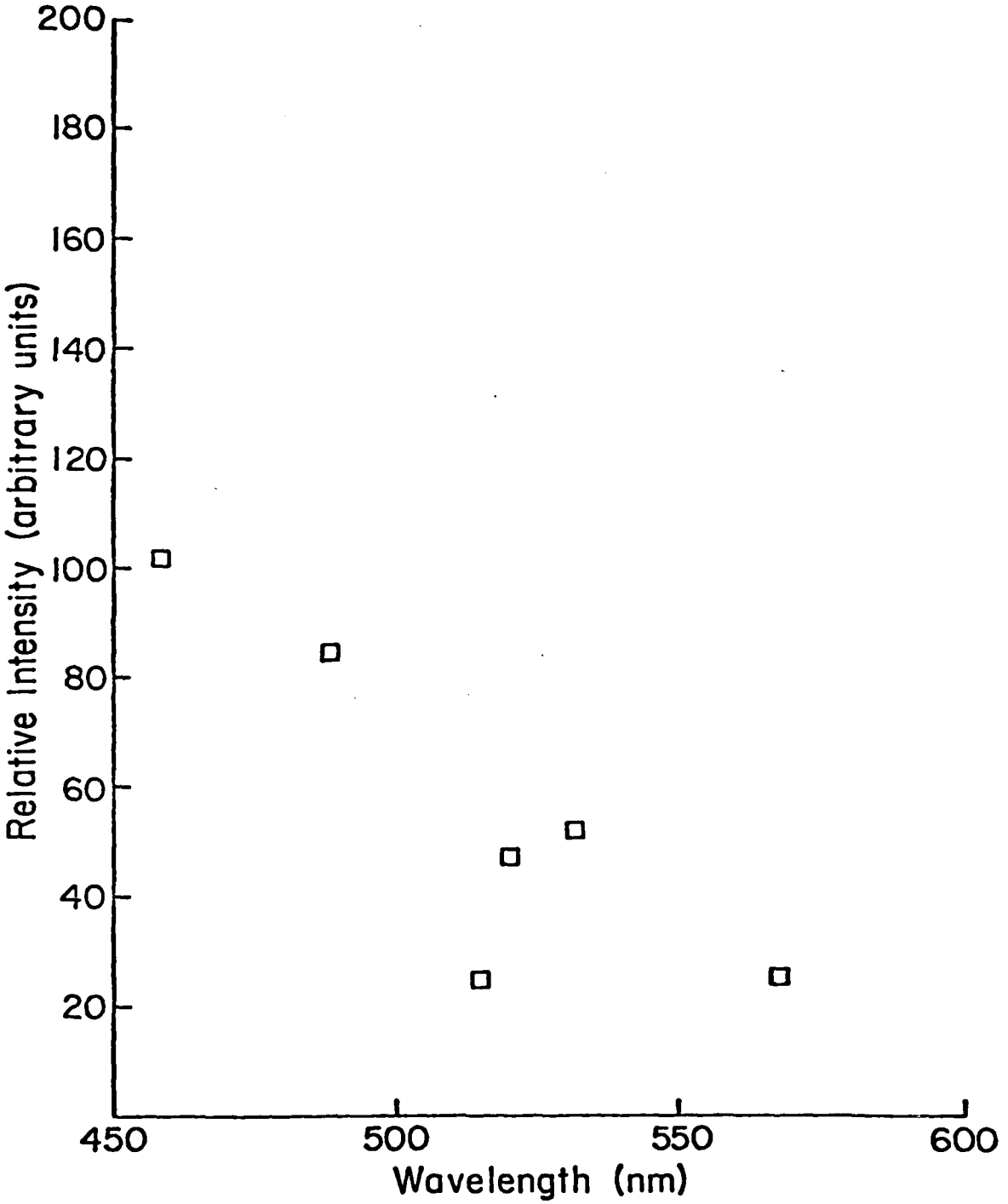

Figure 5. Excitation Profile of CCl_4 Solution of Astaxanthin

Table II. C=C Stretching Mode $V_{C=C}$ for Various Excitation Wavelengths

Excitation Wavelength Used to Obtain the Raman Spectrum	C=C Stretching Frequency with Simultaneous psec Illumination	C=C Stretching Frequency with no Simultaneous psec Illumination
4579	1524	1524
4880	1528	1524
5145	1522	1523
5208	1522	1524
5309	1521	1524
5682	1517	1524

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